Development of suitable ferroelectric nanocomposites in thin film form for energy applications

A Synopsis (Approx. 5000 words)

Submitted by

Eheta Samul Kadir

Under the supervision of

Dr. Rabindranath Gayen

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Department of Physics

Presidency University

Kolkata

Registration no. – 18RS09160149

Email: ehetasamulkadir1@gmail.com

Date of Registration – 28.08.2019

DECLARATION

I hereby declare that the dissertation entitled "**Development of suitable ferroelectric nanocomposites in thin film form for energy applications**" to be submitted for the degree of Doctor of Philosophy is my original work and the dissertation has not formed the basis for the award of any degree, diploma, associateship or fellowship of similar other titles. It has not been submitted to any other University or Institution for the award of any degree or diploma.

Place: Kolkata

Eheta Samul Kadir

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(Eheta Samul Kadir)

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1. Introduction

In recent times flexible ferroelectric thin films of high quality is essential for the prodigious advancement and extensive foreground application in flexible wearable electronic devices, such as, sensors, memory devices and energy harvesting systems [1-2]. In this regard, several organic polymers being mechanically robust and structurally diverse are very popular as flexible ferroelectric materials [3]. Polyvinylidene fluoride (PVDF) being a semi-crystalline electro-active polymer, has emerged as promising material for flexible devices, such as sensors, actuators, electromechanical energy harvesting systems due to its unique piezo, pyro and ferroelectric properties [4-6]. Now improvement of ferroelectric properties by introducing various nanofillers without affecting its mechanical strength has gained immense importance in recent times [7]. In this regard tri-phase composite combining graphene nanosheet with PVDF becomes a good option for ferroelectric application. Graphene oxide (GO) or reduced graphene oxide (r-GO) which is a two dimensional honeycomb structured network of carbon atoms with sp^2 hybridization and abundant surface functional group, have been used as reinforcements in PVDF-composites. GO contains high specific surface area of about 2600-3200 m^2/g and forms conducting network while composites with PVDF enhancing its dielectric polarization as well as the dielectric permittivity [8]. On the other hand zinc oxide (ZnO) has been utilized greatly due to their fine ferroelectric and piezoelectric properties in energy storage and harvesting devices. Also the heteroatom-doped and/or nanocomposited ZnO structures show enhanced ferroelectric characteristics. Also ZnO helps in reducing GO to r-GO and prevents the agglomeration of GO or r-GO sheets through Coulomb

interaction with its surficial functional groups in tri-phase composites [9]. Large amount of charge accumulation at the polymer/nanofiller interface in high dielectric composite materials reinforced with nanostructures is a major problem for their electronic device applications. So manipulation of induced interface polarization at the polymer/nanofiller interface using GO conducting network can be beneficial for application in flexible polymer based devices.

Piezoelectric energy harvesting is a technology may fulfil necessity of energy by converting abandoned mechanical energy into useful electrical energy [10]. This energy can be utilized for powering up of various low power electrical and electronic instruments [11-12]. There are several materials with high piezoelectric coefficient like zinc oxide (ZnO), barium titanate ($BaTiO_3$), lead zirconate titanate (PZT) etc. [13]. But their brittle nature don't allow them to undergo enough mechanical force. So in this context flexible piezoelectric materials appears as an alternative to them. PVDF is a piezoelectric material belongs to flexible polymer group. Moreover high sensitivity, easy processing technique, chemical stability makes them further fruitful [14]. Although polymer substances possess multiple relaxation process, but high relaxation time makes them suitable for retaining power for a longer period of time. Also ZnO provides better crystallinity to PVDF polymer which aids in better conversion of energy [15]. On the other hand, conducting nature of GO leads to better transport. Also insertion of GO enhances β-phase content in PVDF. While adding both ZnO and GO, significant modification in interfaces between host PVDF and ZnO/GO filler has also been observed which flourishes β-phase content in PVDF polymer attributed to the reduction in size of crystal structure. ZnO helps in formation of reduced GO (r-GO) from GO due to electrostatic interaction between surface functional groups. As a result, the β-crystalline tri-phase PVDF/ZnO/GO polymer nanocomposite membranes with little amount of ZnO and GO nanofillers can produce higher output voltage and current under mechanical vibrations making them best suited for piezoelectric energy harvesting applications [16]. PVDF is a polymer with a reported band gap 5.66 for indirect transition and 4.96 for direct transition [17]. Also it authorizes us to use them in arbitrary rough surfaces. But due to very high resistive nature, low mobility and high accumulation of charge particles in PVDF, only few generated charge carriers are able to reach electrode causing less photocurrent [18]. Graphene Oxide (GO) and reduced graphene oxide (r-GO) are considerable materials having many remarkable features like excellent conductivity, enormus mechanical strength, good thermal conductivity, molecular barrier and interesting optical properties. Reports suggest that inclusion of GO into host PVDF provides better conductivity, response time, responsivity and conductivity [19]. Also GO provides better crystallinity which allows a faster response. So PVDF/GO turns out to be a flexible broadband photosensitive material [20].

Here we discussed in detail synthesis of PVDF and its various nanocomposites in chemical route by sol-gel spin coating technique. Formation of PVDF and its nanocomposites have been confirmed from microstructural studies X-ray diffraction (XRD), Fourier transformed infrared(FTIR) and X-ray photoelectron spectroscopy(XPES). After formation of PVDF various nanomaterials like ZnO and/or GO has been added for improvement of its dielectric, ferroelectric and piezoelectric properties.

2. Literature review

Recently ferroelectric polymers have grabbed enormous interest due to their light weight, being cheap, easy to process and compatible with different surfaces. PVDF is one those such polymer belongs to organic group recently going through extensive researches. It has many prominent features like ferroeltric, dielectric, piezoelectric and pyroelectric behaviour. Due to superior ferroelectric nature and high dielectric strength of PVDF they have been used in high power density storage applications [21]. Moreover their flexibility allows them to use even rough, arbitrary situation. They have gained interest to be used in flexible memory devices, electronic skin, transducers etc [22]. Their tunable ferroelectric property makes them further interesting material for ferroelectric and piezoelectric applications [23]. Having spontenous polarization in PVDF, it qualifies as a potential substance for application in memory devices [24]. Again being a pyroelectric material itself PVDF has been used in flexible kind of temperature sensing devices [25]. But PVDF solely displays many shortcomings like slow response time, high dielectric loss, low current density being a polymer. There are countless composites have been synthesized with PVDF as base material. ZnO nanoparticle is one those such materials which have been used extensively as a dopant. Reports suggests that with inclusion of ZnO in PVDF dielectric constant shows an enhancement compared to pristine PVDF so that can be beneficial for storage applications [26]. Ferromagnetic property also seems to improve while adding CuO into PVDF matrix [27]. Energy storage performance of PVDF also improved by introduction of Fe_3O_4 [28]. Further improvement in ferroelectric, energy storage and energy harvesting performance is perceived by introduction of a third phase into it [29]. Due to retaintive capacity of PVDF they are potential substance to be used in memory devices [30]. Recently heterojunction prepared by PVDF/MoS_2 is capable of showing excellent hysteresis property which leads to development of tremendous memory devices[31]. Owing to their piezoelectric nature PVDF has been used excessively as a layer of various energy harvesting devices [32]. But being an organic polymer it can't convert abandoned mechanical energy into sufficient electrical energy due to low efficiency. So we are left with an option of blending PVDF with material having high piezoelectric coefficient. Nanomaterials with high piezoelectric coefficent like $BaTiO_3$, ZnO, PZT have been incorporated into PVDF for better output energy from an abandoned source of mechanical energy [33-35]. Recently graphene oxide(GO) or reduced graphene oxide (r-GO) have been used exceedingly for its mechanical, thermal, electrical and barrier properties [36]. GO modifies many crucial properties of PVDF like its dielectric, piezoelectric and pyroelectric behaviour [37-38]. PVDF also reported to have high band gap ~ 5.5 eV [39]. So PVDF is able to absorb high energetic radiation. Being a dielectric polymer substance a little amount of current is obtained at the electrodes. So to enhance its sensitivity GO has been used as a dopant material by increasing it's conductivity and effective interface [40].

3. Experimental

3.1 Materials used for synthesis

Poly (vinylidene fluoride) (Sigma-Aldrich), N-N-Dimethyl formamide (DMF) (Sigma Aldrich, Purity>99.5%), Acetone (Merck, Purity>98%), 2-Propanol (Merck, Purity> 99%), GO powder (Sigma-Aldrich, Purity>99%), Zinc acetate dihydrate (Merck, purity> 98%), Diethanolamine (DEA) (Sigma-Aldrich, purity> 98%),

3.2 Synthesis procedure

PVDF film deposition

0.64 gm PVDF powder was taken in a conical flux and mixed with 2 ml DMF and 2 ml acetone. This mixture is then rigorously stirred on a hot plate magnetic stirrer for 1 hour at a temperature of ~ 60^0C. As a result a thick, viscous, transparent solution is obtained. This solution is then spin coated on fluorine doped tin oxide (FTO) coated substrate or flexible Polyethylene terephthalate (PET) substrate depending upon nature of application. It is spin coated by a manual programmable spin coater (Apex Instruments) for 1 minute at a rotation speed ~ 3000 rpm. This thin layer is then heated at ~ 120^0 C for 10 minutes to avoid unwanted compounds. In this way flexible, transparent, free-standing PVDF film is synthesized.

3.3 PVDF composite film deposition

For synthesis of composite films two separate solutions of ZnO and GO along with PVDF solution are prepared. 0.5 M (5.48 gm) zinc acetate dihydrate was mixed into 50 ml isopropanol and stirred on a magnetic stirrer for 60^0 C for 1 h. This solution is stirred for another day at room temperature to obtain proper mixing. After preparing this solution, it is kept intact to earn it in precipitated form. Then it is kept at hot air oven at ~120^0 C for few minutes to achieve in powder form. This compound powder is then annealed at ~ 450^0 C in the furnace to remove unwanted compounds and obtain pure zinc oxide (ZnO) in powder form. Then 2 mg ZnO powder is mixed with 25 ml isopropanol and ultrasonicated for 4 h by an ultrasonicator to obtain little whitish transparent ZnO solution.

On the other side 2 mg of GO powder is dissolved into 50 ml of isopropanol to prepare solution. This mixture is then ultrasonicated for 4 h. This solution is then filtered by filter paper to obtain clear transparent GO solution. To prepare composite films, ZnO and/or GO solution is mixed to PVDF mixture produced as mentioned above to a ratio of 10% (v/v). This combined mixture is then spin coated and dried as proposed earlier to get free standing, flexible thin films of composite materials.

4. Result and discussions

4.1 Microstructural studies

The surface morphology of the PVDF and its composite free-standing films were recorded by a CARL ZISS (EVO LS 10) scanning electron microscope (SEM) operated at 25 kV. Fig. 1(a–d) (FESEM images) shows the surface morphologies of PVDF composite membranes. The surface morphology of the pristine PVDF free-standing membrane is relatively smoother compared to those of the nanofiller (ZnO and GO) incorporated PVDF polymer matrix. The modification of surface with enhanced roughness and porosity is also evident from the top view microscopic image attributed to the presence of ZnO and GO nanofillers in PVDF matrix.

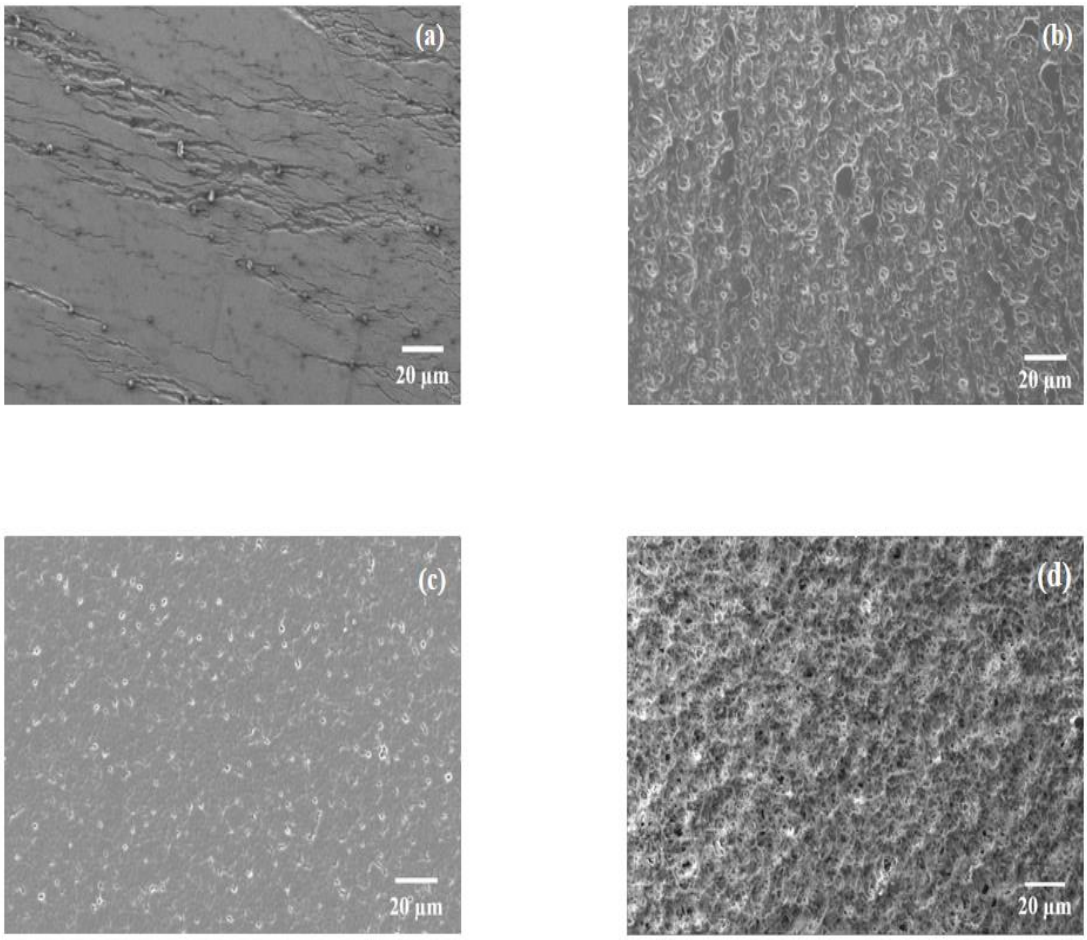


Fig. 1 SEM images of (a) PVDF (b) PVDF/ZnO (c) PVDF/GO and (d) PVDF/ZnO/GO

X-ray diffaraction (XRD) pattern of PVDF and its composites are shown in fig. 2. All of those samples are showing XRD peak at ~ 20.2^0 correspionding to β-phase of PVDF which is highly polar. There is another small peak at ~ 18^0 is observed which is attributed to α-phase of PVDF implying presence of this phase to a smaller amount. After inclusion of dopants peaks seem to sharpen ensuring better crystallinity of those composites.

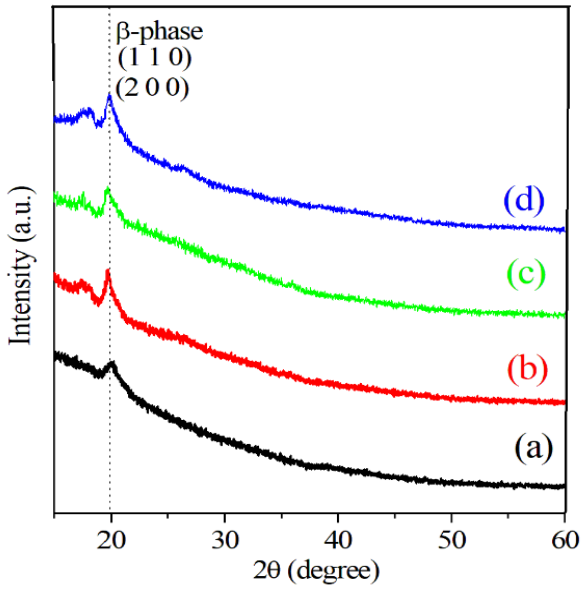


Fig. 2 XRD pattern of (a) PVDF (b) PVDF/ZnO (c) PVDF/GO and (d) PVDF/ZnO/GO

Fourier transformed infrared (FTIR) spectroscopy is an appreciable technique to get significant insight about molecular bonding enviornment a material. FTIR spectrum of all nanocomposites are presented in fig. 3. Typical absorbtion bands of PVDF are present in all composite membranes indicating there is no such structural deformation after filler inclusion. The strong absorption bands located at 839 and 878 cm−1 is attributed to the H-C-H rocking and F-C-F asymmetric stretching mode of vibration, respectively [41]. Absorption bands arising out of C-C asymmetric stretching mode, F-C-F symmetric stretching mode, C-F out-of-plane deformation, and H-C-H wagging vibration are observed at 1072, 1170, 1270 and 1400 cm^{-1} respectively [42]. For PVDF/GO and PVDF/ZnO/GO composite polymer membranes, a weak absorption band is prominent at 1727 cm−1 which is attributed to the C=O stretching mode of vibration for carbonyl and carboxyl group of GO sheet [43]. For the composite membranes with ZnO nanofillers (PVDF/ZnO and PVDF/ZnO/GO membranes), additional small absorption band for Zn-O stretching mode is observed at 447 cm^{-1}. Various crystalline phases of PVDF have also been identified from the FTIR spectra of the nanocomposite membranes within the wavenumber range 400–1500 cm^{-1} [44]. The IR absorption bands appeared at 512 cm−1, 839 cm−1, and 1170 cm−1 for all nanocomposite membranes can also be attributed to the β-crystalline phase of PVDF but not so conclusively. The strong absorption band at 878 cm^{-1} which became more prominent in PVDF/ZnO/GO composite membrane can be assigned as α-crystalline phase of polymer matrix as evident from XRD pattern.

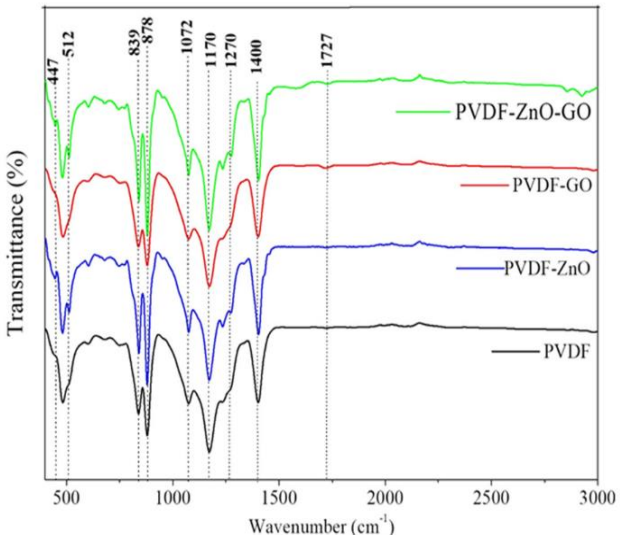


Fig. 3 FTIR spectra of PVDF and its composites membranes

Analysis of XPS spectra confirms presence of C, F and O in PVDF and PVDF/GO membranes and presence of C, F, Zn and O in PVDF/ZnO and PVDF/ZnO/GO samples. The C-C (sp^3-C) peak at 285.6 eV of PVDF shifted towards 284.5 eV for PVDF/ZnO, PVDF/GO as well as PVDF/ZnO/GO films which could be assigned to C=C (sp^2 C). Although there are both C-C and C=C bonds in PVDF/ZnO/ GO composite film. Furthermore, the peak for C-H bonds at 284.3 eV in PVDF is superimposed with C=C peaks (~284.5 eV) for composite PVDF films which can also be confirmed by the increase in full width at half maximum (FWHM) of C=C peaks for composite PVDF films as compared to the FWHM of C-H peak for pristine PVDF film. Therefore, the bonding environment of PVDF is greatly disturbed through compositing it with ZnO, GO and ZnO/GO. This can also be confirmed by the modification in morphology of composite PVDF films as observed under SEM images. The disappearance of C-O peak around 293.5 eV, due to presence of adsorbed oxygen content in PVDF film, could have been caused by the introduction of ZnO and/or GO in it. ZnO and GO act as oxygen acceptor in the composite film in forming O-C-O and F-C-O. The disappearance of H-C-H peak of PVDF in composite films could be due to the oxidation of some of the H atoms from PVDF. For our case, in the composite PVDF films, the F atoms of PVDF might have bonded with the C atoms from GO or the Zn atoms of ZnO while the H atoms were most likely boned with O atoms. Compositing GO with PVDF helped to form reduced GO (rGO) which is superior in optoelectronic and conducting properties as compared to GO. Henceforth, the observed modification in structural and morphological characteristics might be beneficial for ferroelectric applicability of PVDF composite films.

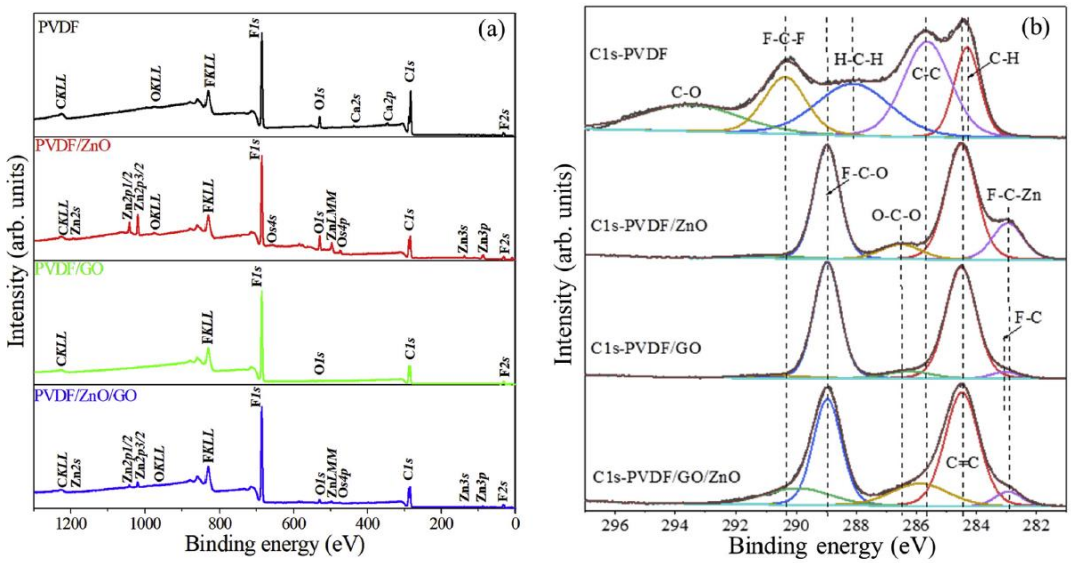


Fig. 4 (a) XPS spectra and (b) deconvolution of PVDF and its composite films

4.2 Ferroelectric and dielectric studies

P-E loop of PVDF and its composites measured at room temperature are shown in fig. 5. P-E loop of the PVDF membrane is significantly altered by incorporation of small amount of GO into it. This may be due to formation of F-C bonds which facilitates better charge transport rather than accumulation. Inclusion of ZnO into host PVDF increases polarization due to formation of F-C-Zn bonds. When both ZnO and GO added into host polymer P-E loop enhances and comparable to that of PVDF/ZnO. Thus PVDF/ZnO/GO is the composite showing better charge transport with relatively high polarization. Polarization for PVDF and its composites are shown in table-1. Ferroelectric polarization of PVDf/ZnO and PVDF/ZnO/GO membranes are 15.98 and 14.14 μC/cm^2, respectively at 15 kV/cm electric field. Such excellence can be attributed to the porous morphology of the composite membranes having abundant interfaces.

Table I

	P (μC/cm^2) at 15 kV/cm	E_d (x104 J/m3)	ε' (at 100Hz)	D (at 100Hz)	σ_{AC} (S/m) (at 1 MHz)
PVDF	5.94	11.30	47	2.31	3.04×10^{-4}
PVDF/ZnO	15.98	65.50	261	2.69	1.14×10^{-4}
PVDF/GO	0.03	0.06	17	0.46	8.75×10^{-5}
PVDF/ZnO/GO	14.14	61.73	151	1.15	2.52×10^{-4}

The energy density (E_d) has been estimated from the P-E loop using the relation

$$E_d = \oint PdE \quad \text{..... (i)}$$

From the values tabulated in table I it is observed that PVDF/ZnO has highest energy density among tham while PVDF/GO has the lowest implying PVDF/ZnO is more suitable for energy storage application.

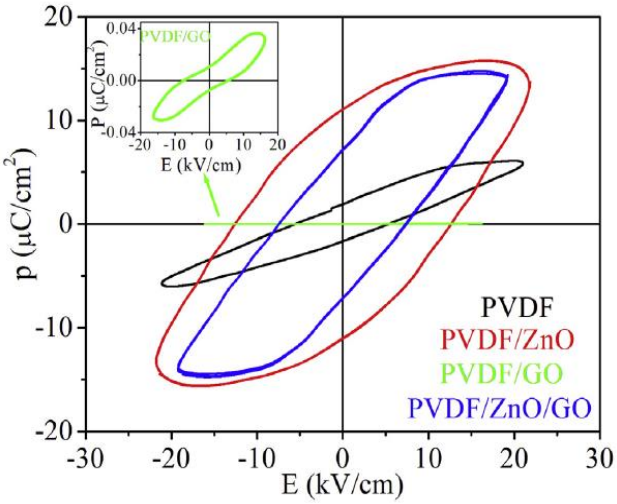


Fig. 5 P-E hysteresis loop of PVDF and its composite films

DC bias dependent impedance spectroscopic study has been carried out at room temperature to get insight about conduction mechanism. Complex impedance of those films can be represented as

$$Z = Z' + jZ'' \quad \text{..... (ii)}$$

Fig. 6(a-d) shows the curves for variation of imaginary part of Z (Z'') with real part of Z (Z') popularly known as Nyquist plot for PVDF and its composites. These plots are fitted by an electrical model circuit consist of a series resistance (R_s) along with two parallel R-C circuits in series. Values of these parameters have been extracted using EIS spectrum analyzing software. Obtained values are represented in table-II. Two different relaxation times are contributions of grain boundaries/interfaces at low frequency and core grains at high frequency [45]. From the insets of fig. 6 it is evident that one relaxation time τ_1 does not vary much with external bias while the other one τ_2 has a change with bias voltage ensuring it must be contribution of those boundaries/interfaces. One of those relaxation time has a very little variation with incorporation of fillers while the other one has significant change referring to the modification of boundaries. In the composite GO network provides an easy pathway for charges while ZnO introduces more interfaces to the composite.

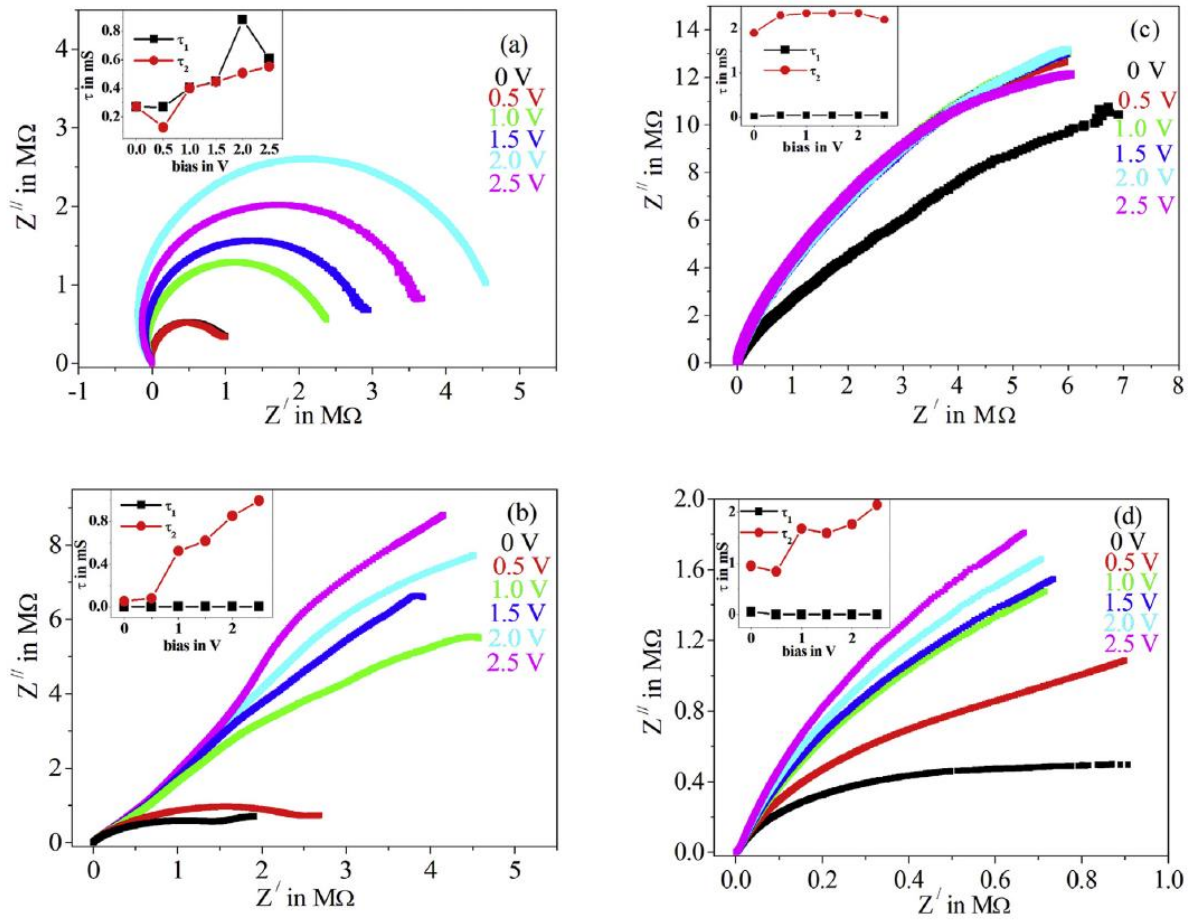


Fig .6 DC bias dependent Nyquist plot for (a) PVDF (b) PVDF/ZnO (c) PVDF/GO and (d) PVDF/ZnO/GO (Inset: variation of τ_1 and τ_2 with external bias of corresponding films)

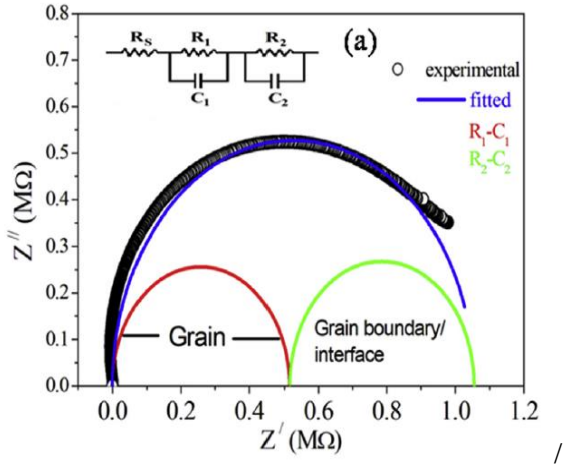


Fig. 7 Fitting of Nyquist plot by model electrical circuit and contribution of different components

Table – II

	$R_s(\Omega)$	$R_1(\Omega)$	$C_1(F)$	$R_2(\Omega)$	$C_2(F)$	$\tau_1=R_1C_1$	$\tau_2=R_2C_2$

						(sec)	(sec)
PVDF	70.1	5.4×10^{5}	4.99×10^{-10}	5.44×10^{5}	4.96×10^{-10}	2.6×10^{-4}	2.7×10^{-4}
PVDF/ZnO	3977.1	1.8×10^{5}	1.03×10^{-11}	1.33×10^{6}	3.99×10^{-11}	1.8×10^{-6}	5.3×10^{-5}
PVDF/GO	443.0	1.5×10^{5}	1.26×10^{-10}	3.13×10^{7}	6.06×10^{-11}	1.9×10^{-5}	1.9×10^{-3}
PVDF/ZnO/GO	640.4	1.0×10^{5}	5.11×10^{-10}	1.01×10^{6}	9.49×10^{-10}	5.1×10^{-5}	9.5×10^{-4}

Complex dielectric constant has also been estimated from impedance spectroscopic study by using the following relation

$$\varepsilon = \varepsilon' + \varepsilon'' = 1/j\omega C_c Z \qquad \text{..... (iii)}$$

Where ε' and ε'' are real and imaginary part of complex dielectric constant respectively and C_c is the capacitance when the sample is replaced by free medium.

Variation of real part of dielectric constant for PVDF with frequency and external bias is shown in fig. 8(a). It shows dielectric relaxation process due to crystalline motion at low frequency at low frequency and non crystalline motion at high frequency. At low frequency ε' decreases rapidly due to easy molecular polarization and attains a peak at 2.7 KHz before being completely saturated at high frequency region indicating β- relaxation process. With increasing bias voltage ε' decreases and the peak shifts towards high frequency region. At high frequency dipoles are unable to follow the switching external field resulting in saturation of ε'. In presence of ZnO inside PVDF membrane dielectric constant is enhanced due to ZnO being polar material itself. When GO is introduced ε' is reduced significantly due to modulation of space charge region at the interfaces. For PVDF/ZnO/GO composite membrane, the zero bias ε' value is slightly less than PVDF/ZnO but higher than pristine PVDF. In the lower frequency region, the ε' value also decreases with external dc bias but the variation is much less compared to PVDF or PVDF/ZnO which clearly indicates the betterment of charge transport through interface by conducting GO network.

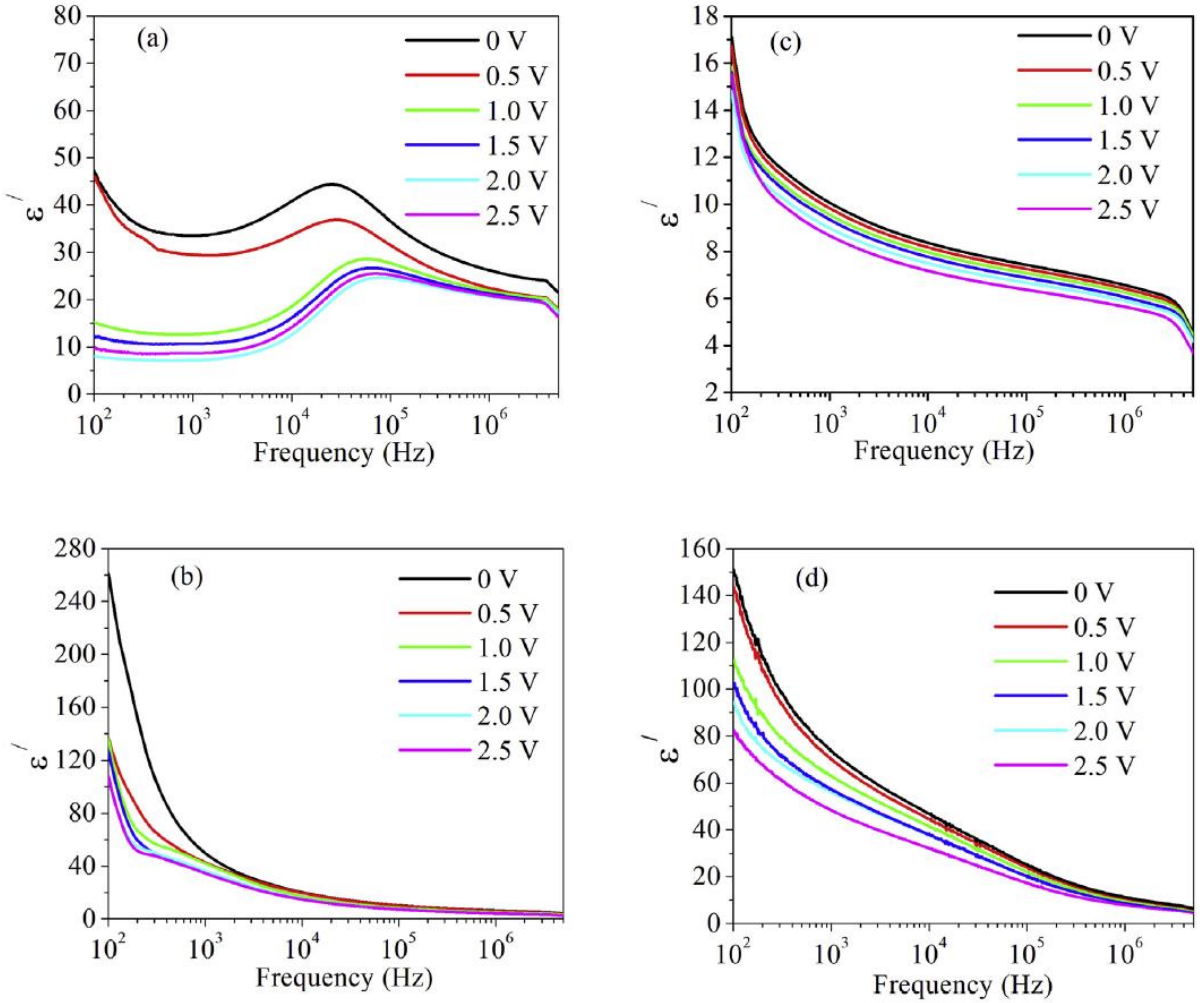


Fig.8 Frequency variation of real part of complex dielectric constant with different dc bias for (a) PVDF, (b) PVDF/ZnO (c) PVDF/GO and (d) PVDF/ZnO/GO membranes

Dielectric loss is an important parameter related to dissipation of power. For all of those composites PVDF/GO shows lowest loss because of better conduction and low accumulation of charges (table-I).

4.3 Mechanical energy harvesting

Different modes of mechanical energy harvesting technique like tapping, stretching and periodic bending have been adopted to study mechanical energy harvesting capabilities of PVDF polymer along with different nanofillers like ZnO, GO and ZnO/GO. The custom-built set-ups for recording the output voltage in open circuit condition using digital oscilloscope (Tektronix-TBS 1072B) and current in short circuit condition by a sourcemeter (Keithley-2450) for each mode of mechanical vibrations. For tapping mode repeated finger tapping is applied on those films. Applied pressure is measured by a calibrated piezoelectric PZT sensor placed under the sample. For bending mode, the free-standing PVDF membranes deposited on flexible PET substrates are periodically bended using a small rod attached to the rotator of a dc motor to generate ac voltage and current signal in the output. For stretching mode,

the two ends of the flexible membranes are kept fixed on two stages connected by a mechanical spring. Repeated stretching and compressing performed manually resulted in ac voltage and current signal in the output. Fig. 9(a-d) shows output voltage of PVDF composite membranes in open circuit condition (V_{oc}) under repetitive finger tapping with average pressure ~ 30 $\pm$ 5 kPa. Average peak voltage values are tabulated in table – III. Similarly fig. 10(a-d) shows average peak current of all of those composites in short circuit condition (J_{sc}). Average peak voltage for pristine PVDF was 15 V which was increased up to 20 V after small amount of ZnO inclusion. But for PVDF/GO membrane there is a fall in output voltage along huge increment in current (fig. 6(c)). For PVDF/ZnO/GO membrane, the average voltage is ~14 V which is comparable to that of pristine PVDF matrix. But the average output current density (Jsc) for PVDF/ZnO/GO membrane is almost 4 times higher than PVDF membranes with maximum deliverable output power (3.1 $\mu W/cm^2$).

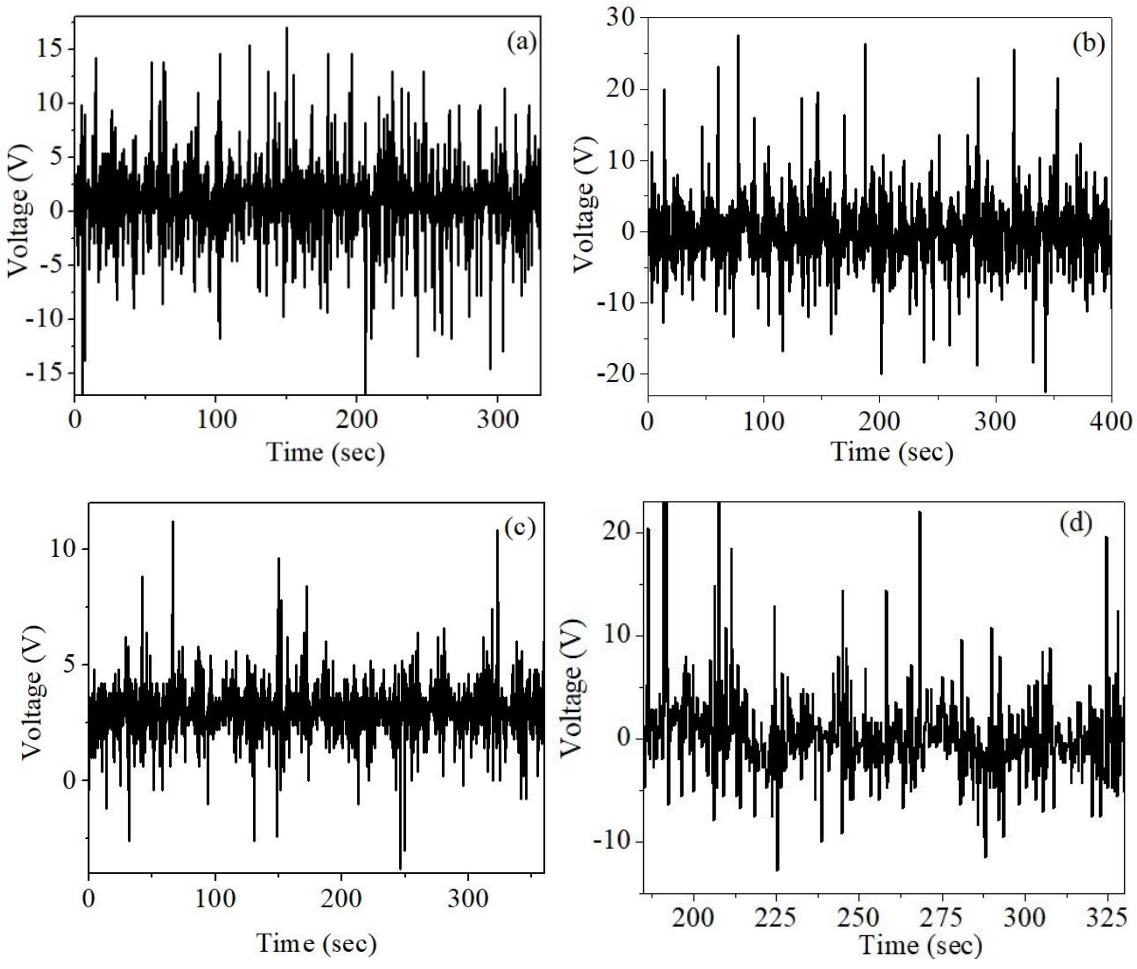


Fig. 9 Measured output voltage signal in open circuit condition for (a) PVDF, (b) PVDF/ZnO, (c) PVDF/GO and (d) PVDF/ZnO/GO composite membranes in tapping mode

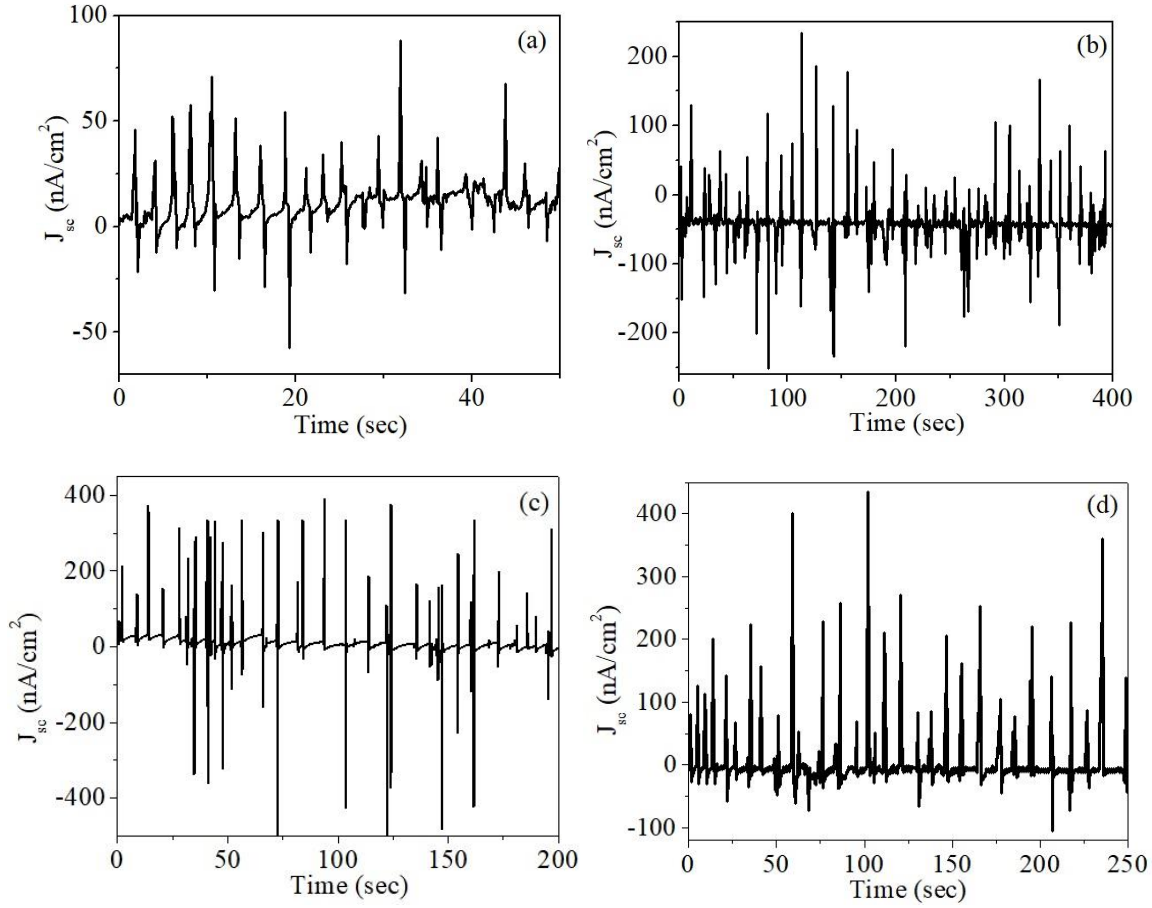


Fig. 10 Measured output current signal in short circuit condition for (a) PVDF, (b) PVDF/ZnO, (c) PVDF/GO and (d) PVDF/ZnO/GO composite membranes in tapping mode

Output open circuit voltage (V_{oc}) and short circuit current (J_{sc}) for all those composites are shown in fig. 11(a-d) and fig. 12(a-d) for periodic bending at a certain frequency. Among all of these membranes PVDF/ZnO shows peak voltage of 6.5 V with small drop of current density (0.5 μA/cm^2). The output current density (Jsc) increased significantly in the presence of GO in composite membranes to 1.1 from 0.6 μA/cm2. But in this mode also the maximum possible output power is demonstrated by the PVDF/ZnO/GO composite membranes (5.4 μW/cm2).

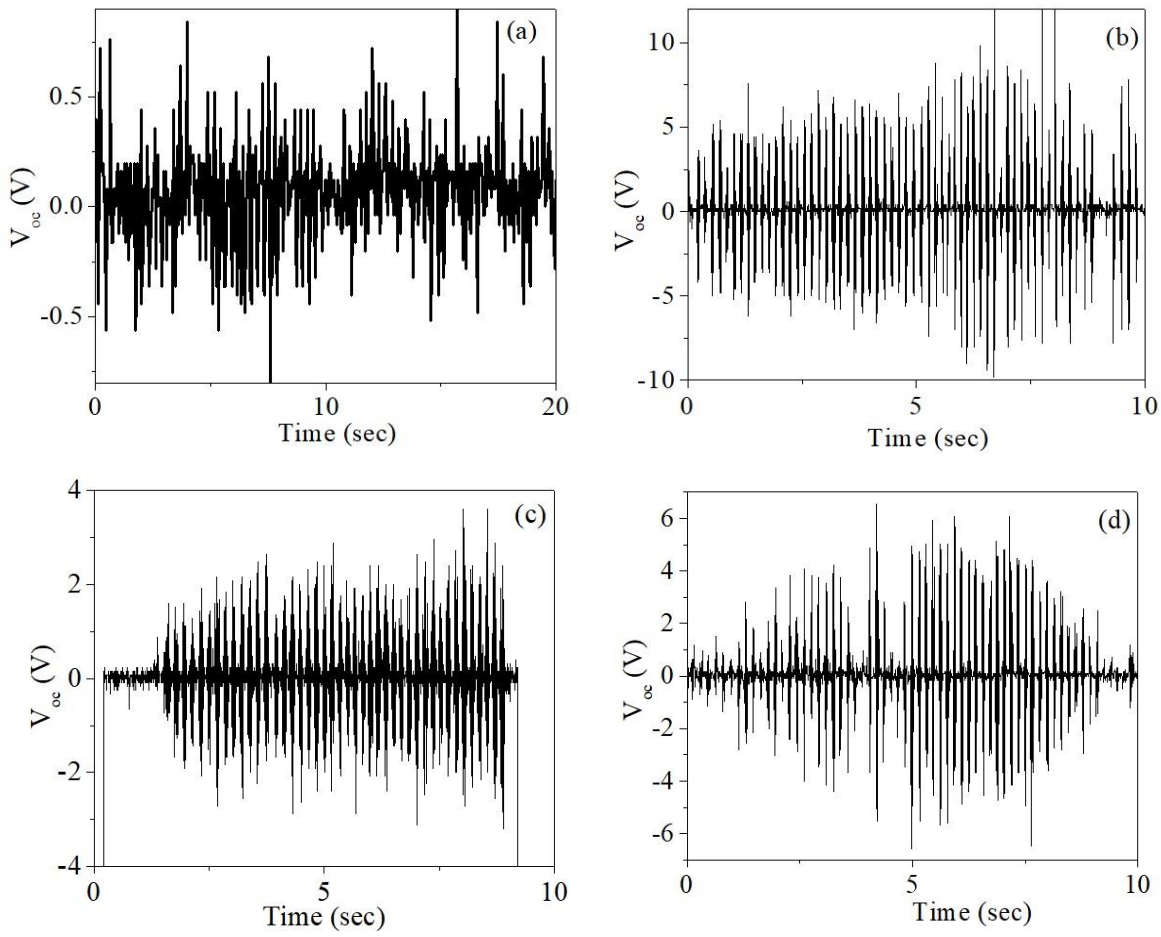
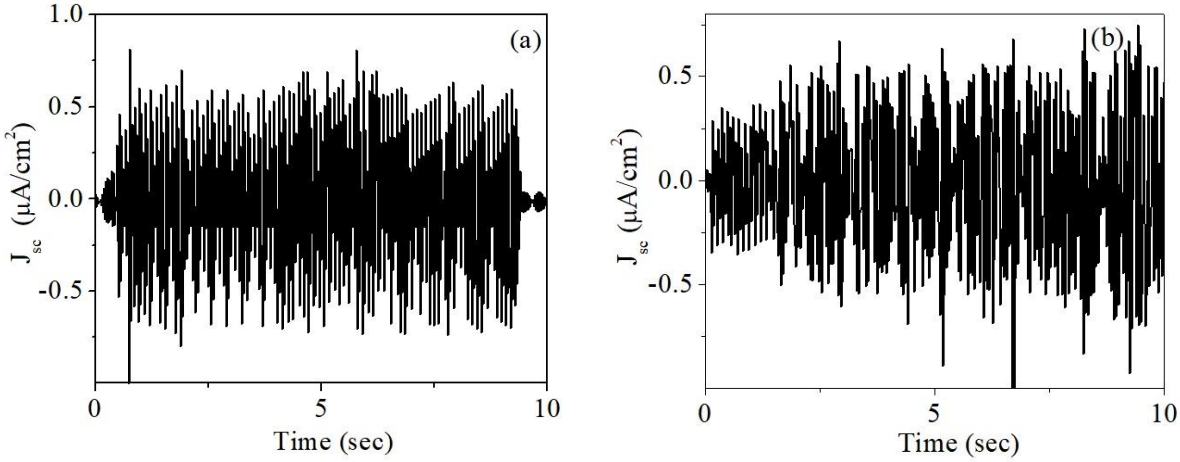


Fig. 11 Measured output voltage signal in open circuit condition for (a) PVDF, (b) PVDF/ZnO (c) PVDF/GO and (d) PVDF/ZnO/GO composite membranes in periodic bending mode



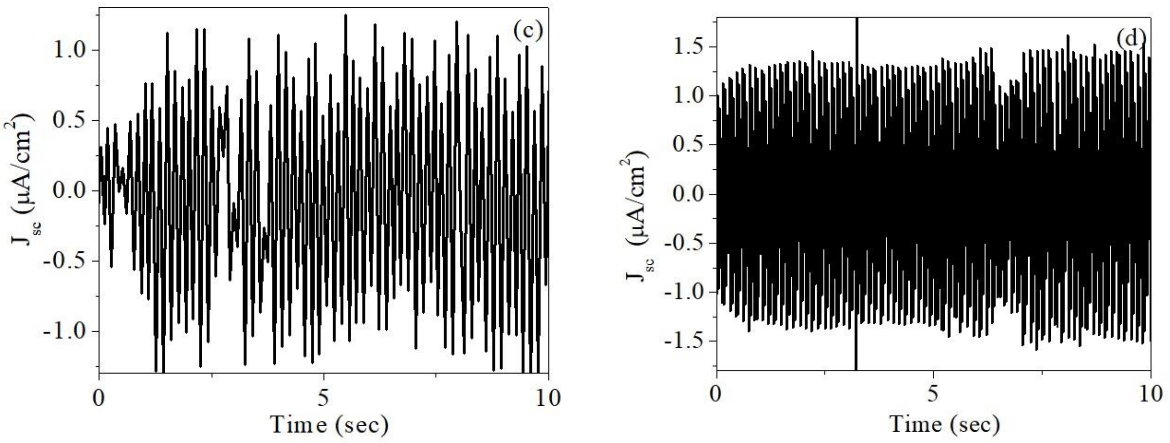


Fig.12 Measured output current signal in short circuit condition for (a) PVDF, (b) PVDF/ZnO, (c) PVDF/GO and (d) PVDF/ZnO/GO composite membranes in bending mode

In stretching mode, the maximum average peak voltage obtained for PVDF/GO membrane is 14 V while the short circuit current density is the maximum for PVDF/ZnO composite. But for PVDF/ZnO/GO membrane there is considerable growth in both short circuit current (0.3 μA/cm^2) and open circuit voltage (10 V) making this composite most efficient mechanical energy harvester with maximum possible output power density ~ 3 μW/cm^2.

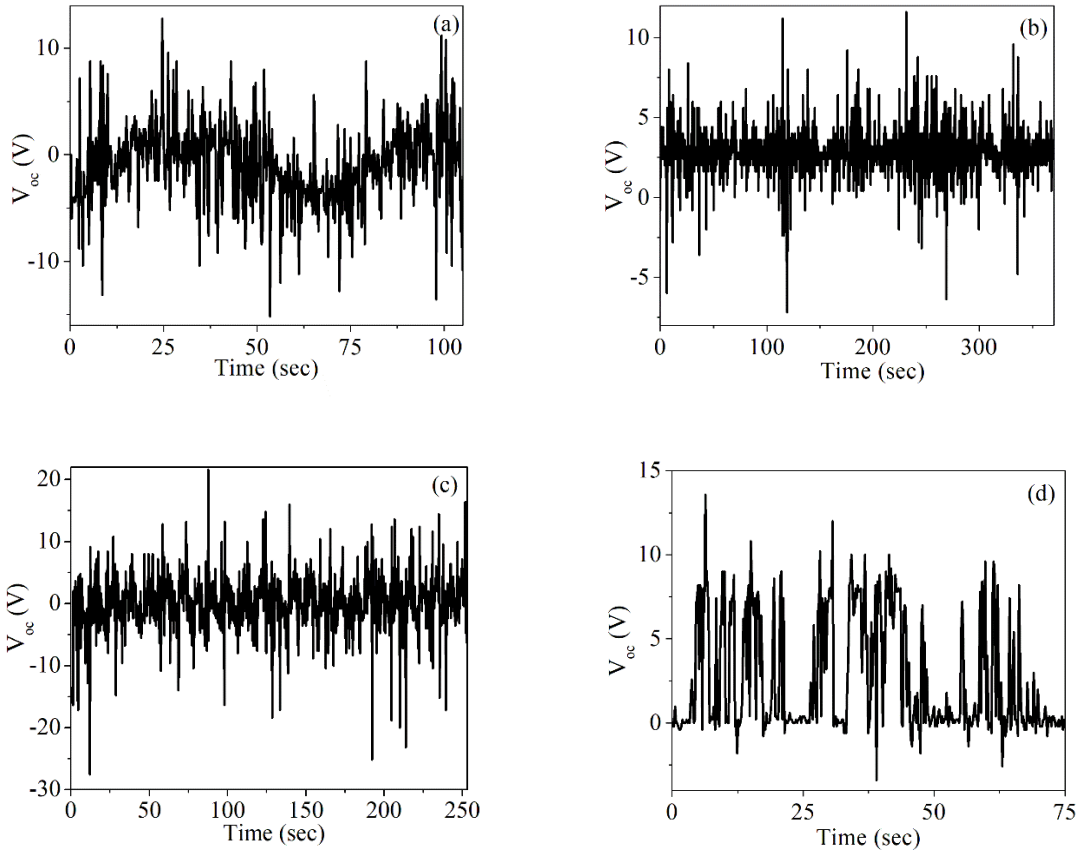


Fig. 13 Measured output voltage signal in open circuit condition for (a) PVDF, (b) PVDF/ZnO, (c) PVDF/GO and (d) PVDF/ZnO/GO composite membranes in stretching mode

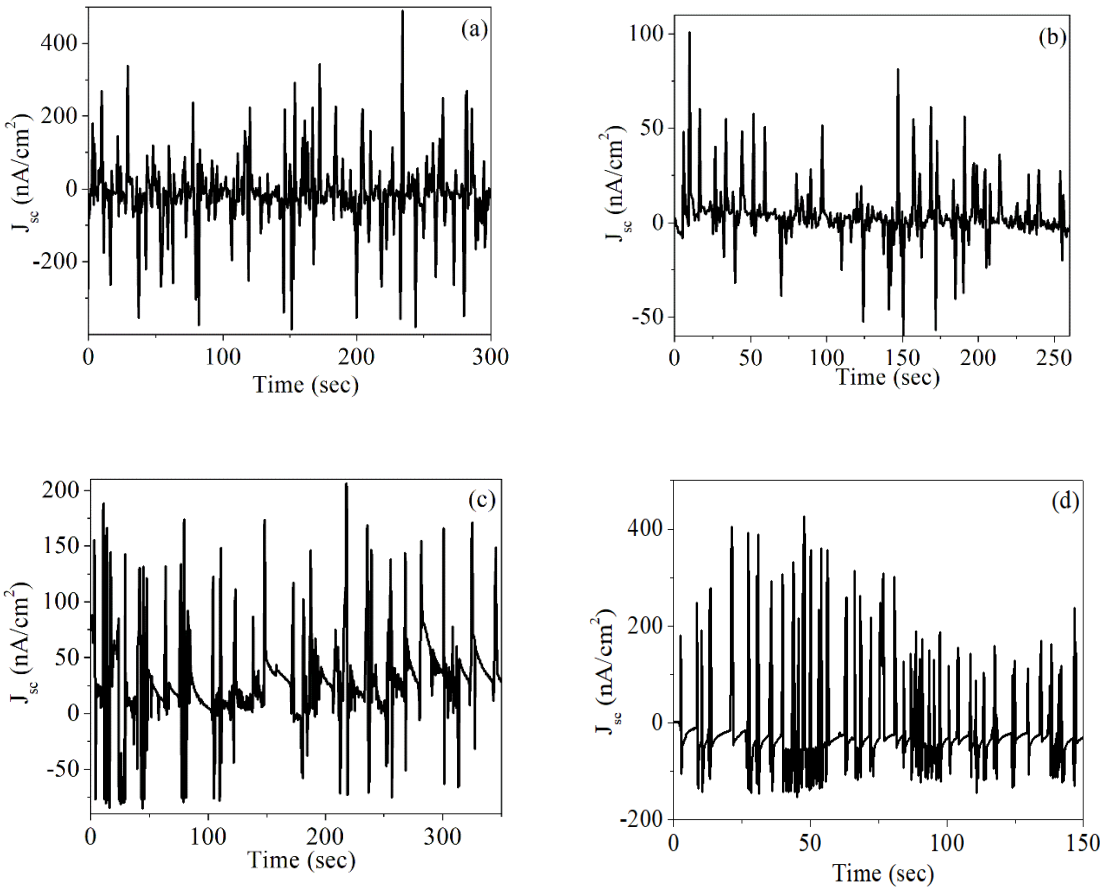


Fig. 14 Measured output current signal in short circuit condition for (a) PVDF, (b) PVDF/ZnO, (c) PVDF/GO and (d) PVDF/ZnO/GO composite membranes in stretching mode

Table – III Average of peak values (amplitudes) of Voc, Jsc and Maximum deliverable output power density of PVDF composite membranes in different modes

	Tapping mode			Bending Mode			Stretching mode		
	Voc(V)	Jsc (nA/cm^2)	Power (μW/cm^2)	Voc(V)	Jsc (μA/cm^2)	Power (μW/cm^2)	Voc(V)	Jsc (nA/cm^2)	Power (μW/cm^2)
PVDF	15	50	0.8	0.5	0.6	0.3	8	255	2.0
PVDF/ZnO	20	125	2.5	6.5	0.5	3.3	8	325	2.6
PVDF/GO	6	325	1.8	2.3	1.1	2.4	14	172	2.3
PVDF/ZnO/GO	14	220	3.1	4.0	1.3	5.4	10	304	3.0

4.4 Flexible photodetector

Figure 3 represents optical absorption spectrum of PVDF and its composites with various GO concentrations measured by UV-Vis spectrometer in the range of 200-800 nm. PVDF and its composites show absorption of a broad band with maximum absorption nearly at 325 nm. For all of those composites a sharp absorption edge is observed at 310 nm. On the other side there is gradual fall in absorption upto almost 800 nm is observed. With increment of percentage of GO doping, there is slight increase in absorption is observed. Maximum absorption is exhibited by the PVDF/15% GO composite. Upper levels of the valence band states in PVDF are combination of the atomic states of C, H and F atom electrons, however 2p electron states of Fare contained in larger amount. On the other hand 2p electron states of those C atoms bonded with F forms the lower levels of conduction band [46].

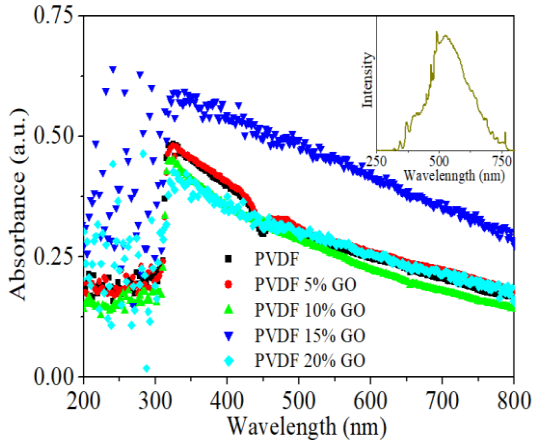


Fig.15 Optical absorbance of PVDF and it's composites and used solar spectrum in the inset

Fig. 16 represents time dependent rise and fall curves of PVDF and its composites with different concentrations of GO illuminated by a solar simulator of lamp power 150 watt while an external bias 10 V is applied across them. The incident broadband spectrum with peak at 525 nm is shown in the inset of fig. 15. For pristine PVDF dark current density is ~ 0.4 μA/cm^{2}for an external bias voltage of 10 V. In presense of light there is gradual increase in current density is observed. In presense of light current increases to ~ 1.0 μA/cm^2. Being a polymer material and semi-crystalline in nature, response time as well as recovery time of the material is slow compared to conventional phodetectors [47]. Being a polymer substance pristine PVDF shows rise time ~ 44 sec. Dark current, photocurrent, rise time for PVDF and its composites are shown in table-4. There is gradual increment in dark as well as photocurrent is observed with incorporation of GO in host PVDF. For PVDF/15%GO composite maximum photocurrent is observed to be ~ 7.5 μA/cm^2. This enhancement in photocurrent is observed due to easy transportation of charge carriers through conducting GO network. With further increment in incorporation of GO amount, photocurrent seems to fall. This is may be due to agglomeration of GO in between grains of host PVDF. Therefore PVDF composites show best performance for a particular concentration of GO inside host. Response time is also seems to be faster while GO has been blended

in PVDF upto a certain fraction known as percoalation thersold. This is due to rapid transit of charge carriers through GO conducting network overcoming potential barriers at the interfaces. For PVDF/15% GO response time is observed to be ~ 21 sec which is much faster compared to pristine PVDF (fig. 17).

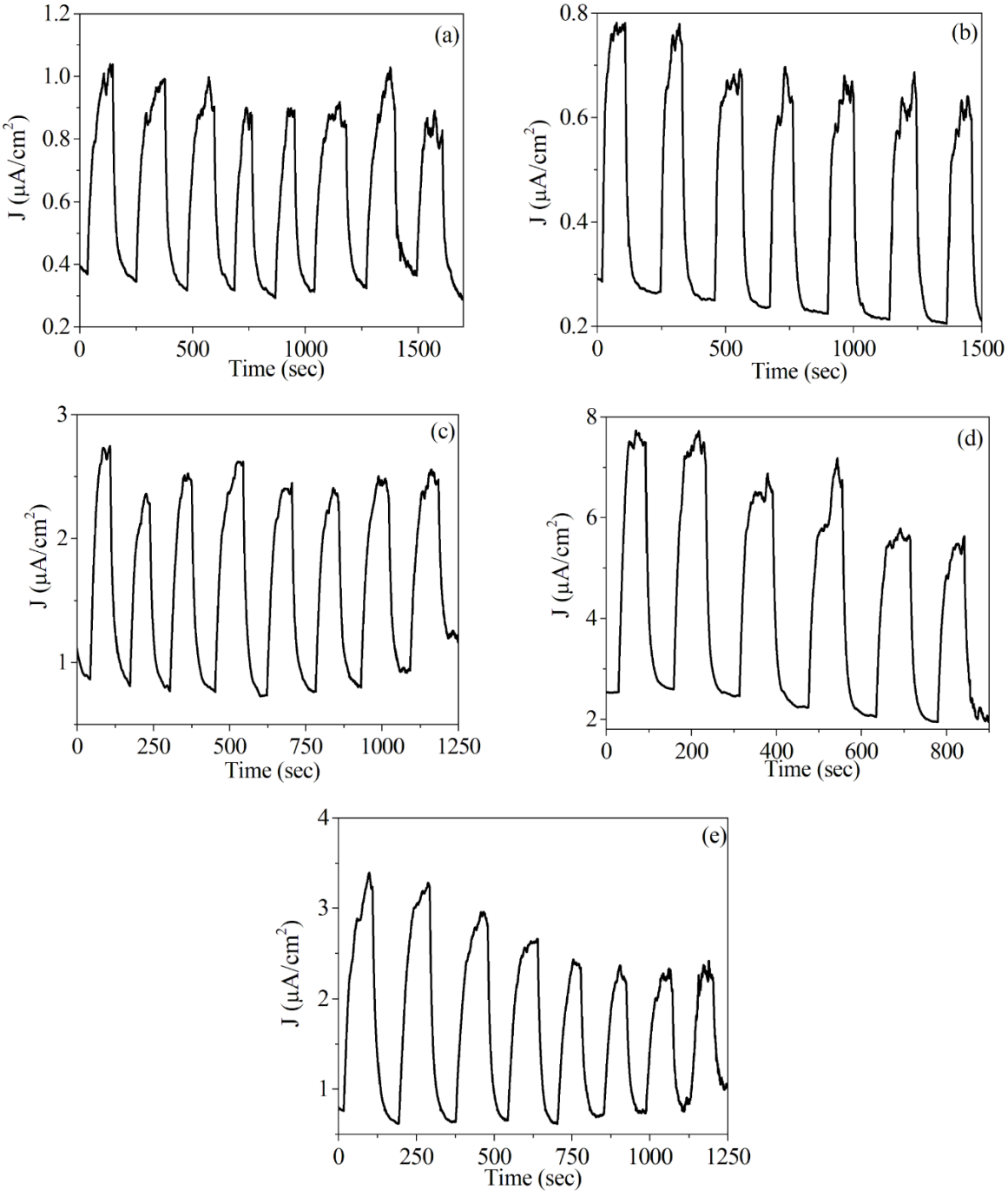


Fig. 16 Photoresponse of (a) PVDF, (b) PVDF/5%GO, (c) PVDF/10%GO, (d) PVDF/15%GO and (e) PVDF/20%GO

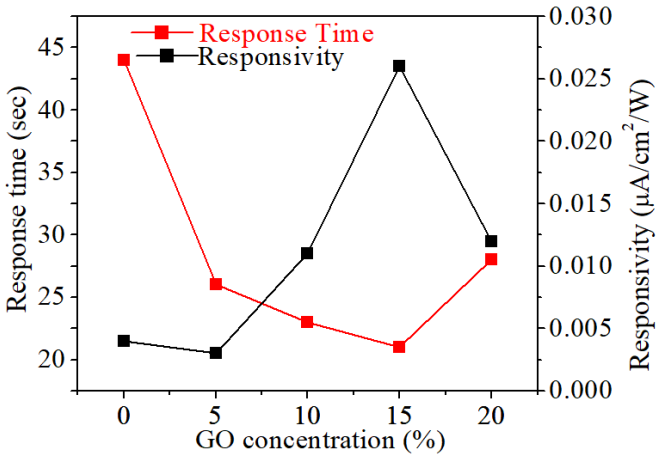


Fig. 17 Response time and Responsivity of PVDF and it's composite with different GO concentrations

Table IV

	J_{light}-J_{dark}(μA/cm^2)	Saturation time(τ)(sec)	Responsivity (μA/cm^2/W)	J_{dark} (μA/cm^2)
PVDF	0.6	44	0.004	0.3
PVDF/5%GO	0.5	26	0.003	0.2
PVDF/10%GO	1.7	23	0.011	0.7
PVDF/15%GO	4.0	21	0.026	2.2
PVDF/20%GO	4.0	28	0.012	0.6

PVDF being a flexible polymer itself can be used in arbitarary surfaces also. Photoresponse of PVDF and it's composites are also measured when those substances are placed in bend situation and are shown in figure 18(a-e).For PVDF in ordinary condition photocurrent is ~ 0.14 μA/cm^2 which arises to be ~ 0.24 μA/cm^{2}in bend situation. As concentration of GO is enhanced, there is rise in both dark and photocurrent is observed. For PVDF/15% GO maximum photocurrent is observed which is ~ 0.2 μA/cm^{2}in normal situation which rises to ~ 0.45 μA/cm^2 when placed in bend situation. In such stressed situation both dark and photocurrent seems quite higher compared to that in released situation for all of those composites. PVDF is a well-known piezoelectric substance. So in stressed condition internal dipole are dislocated which produces an additional electric field inside the material.Apart from external applied electric field, this additional interior electric field provides better movement of charge to Ag electrodes. As a result in rough situation better photo-detection is observed by all of those composites. Among them PVDF/15% GO turns out to be best performing device.

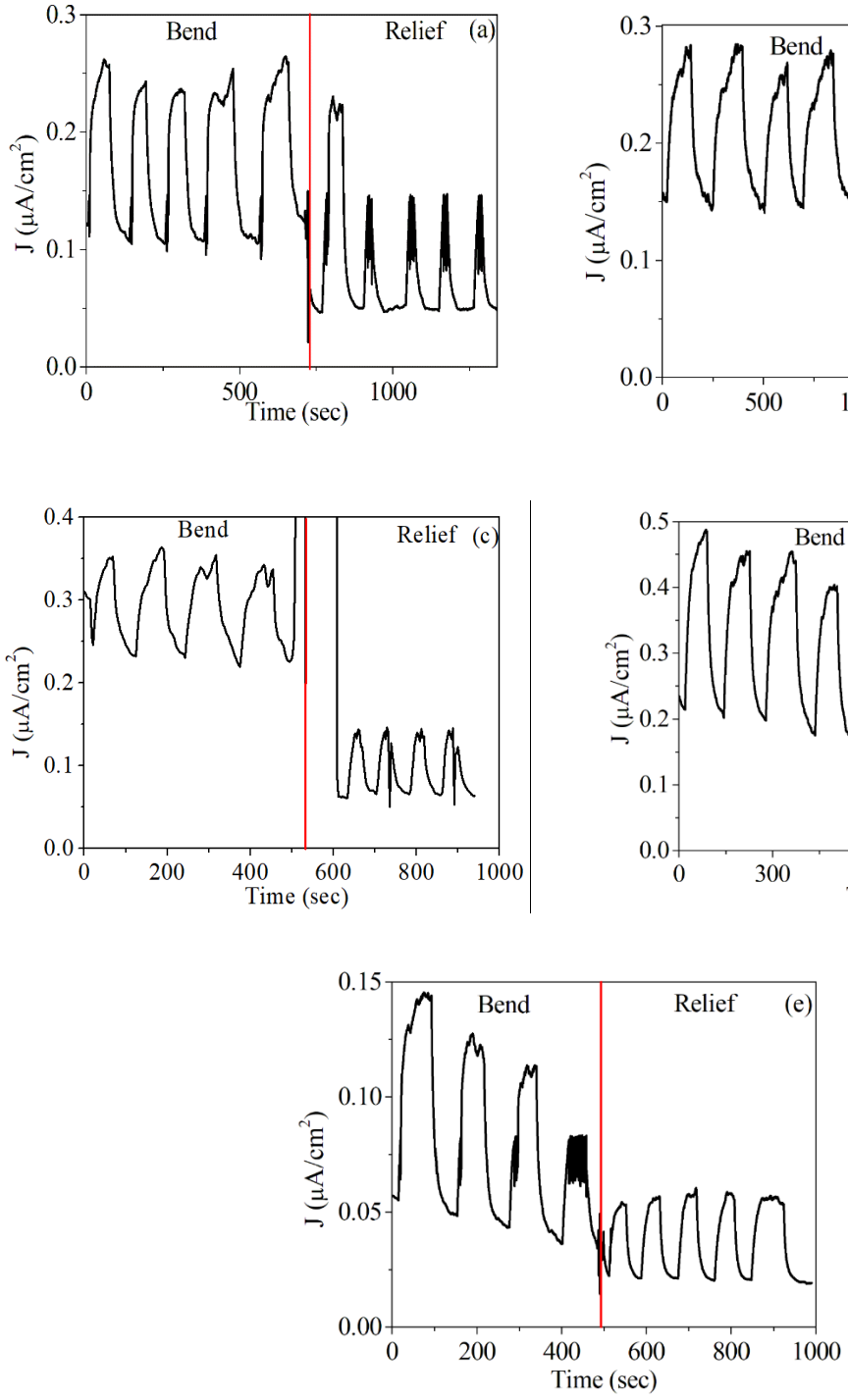
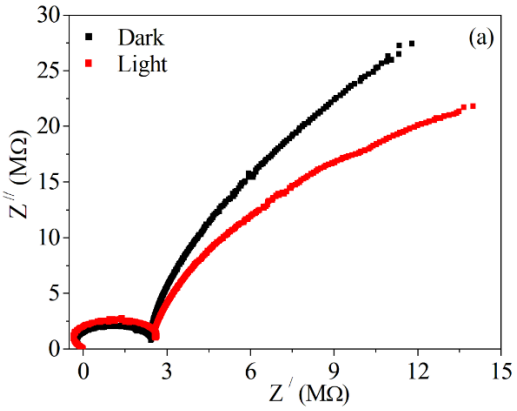
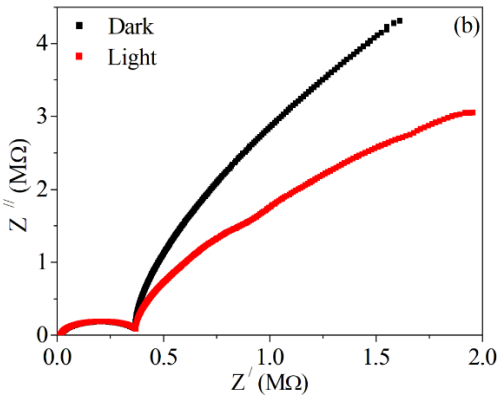


Fig. 18 Photoresponse of (a) PVDF, (b) PVDF/5%GO, (c) PVDF/10%GO, (d) PVDF/15%GO and (e) PVDF/20%GO in bend and released situation

From experimentally obtained impedance spectroscopic data we have showed variation of imaginary part of impedance ($Z^{//}$) with real part of that ($Z^{//}$) popularly known as Nyquist plot in dark and illuminated condition in figures 9(a-e). The plot splitted in two semicircles manifesting contributions

arising from different parts of the sample. According to Koop's phenomenological theory polycrystalline material is consist of high conducting grain separated by relatively low conducting grain boundaries [48]. Also there will be small contributions arising from electrode interfaces or defect sites. But to avoid unnecessary complications we only take into account the effects of grains and boundaries. The high resistance of these substances at low frequency is assumed to be the contribution of the grain boundary while that at high frequency is assigned to grain contribution. Because the dipoles generated due to interfacial polarization able to flip only at low frequency region. At high frequency region contribution of grains become prominent. In presense of light one segment assigned to grain boundary shows significant change while the other one remains unaltered. This fact suggests that in presense of light the core grain is unaffected. But the boundaries where GO nanoparticles are located exhibit contrasting behaviour in presense of light due host-filler modification of boundary. As concentration of GO is enhanced, enhanced effect of light is observed. Because now photo generated carriers experience less obstruction at the boundaries due to formation of conducting network. Beyond percolation thersold effect of light also drop. These results verify GO filler greatly modifies potential barriers at boundaries which provides better conductivity for the nanocomposites.





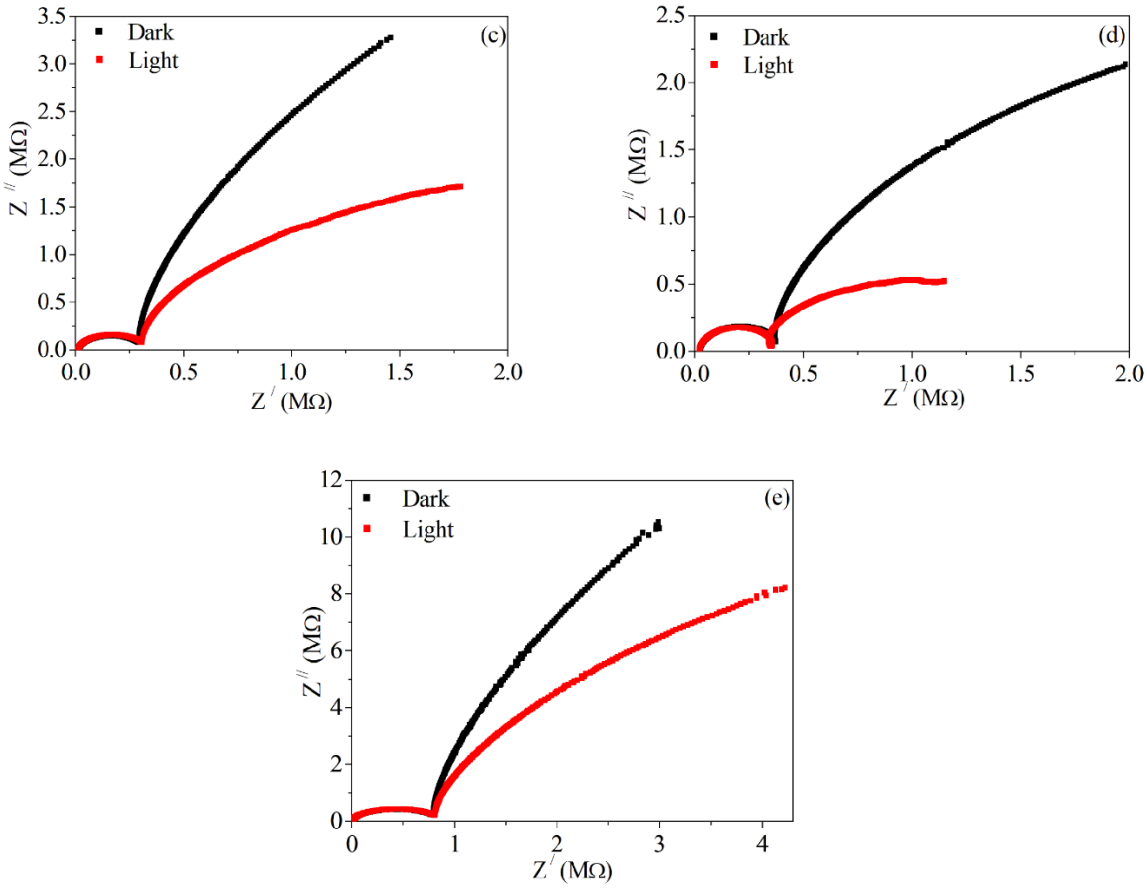


Fig. 19 Nyquist plot for (a) PVDF, (b) PVDF/5%GO, (c) PVDF/10%GO, (d) PVDF/15%GO and (e) PVDF/20%GO at dark and illuminated condition

5. Conclusion –

We have sucessfully synthesized PVDF and its various nanocomposites in free-standing, flexible, thin film for by sol gel spin coating method. Fabricated nanocomposites are better performing candidates in numerous aspects. PVDF/ZnO composite arises out to be best performing material for storage application while PVDF/ZnO/GO shows better storage along with better transport feature. The tri-phase composite PVDF/ZnO/GO proves to be the substance with best energy harvesting capability. Although PVDF is capable of showing photo responsive behaviour but PVDF/GO composite shows better performance due to generation of easy pathway for generated charge carriers. Among them PVDF/15%GO is the composite with best performance amongt them. Response time, responsivity, detectivity also seems to improve by such inclusion.

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